

**CORRELATION OF COAL PROPERTIES WITH HYDROLIQUEFACTION
REACTIVITY: A BRIEF REVIEW**

Robert M. Baldwin
Chemical Engineering and Petroleum Refining Dept.
Colorado School of Mines
Golden, CO 80401

ABSTRACT

Since the earliest days of coal liquefaction processing and research, the desirability of correlation of coal properties with coal reactivity under direct hydroliquefaction conditions has been recognized by coal scientists. This article traces the history of reactivity correlations from the earliest work of Bergius through the classic work at the Bruceton Bureau of Mines during the 1940's to the most recent advances in this subject. Particular emphasis in this review is placed on an examination of the contributions of Professor Peter Given and his co-workers. Reactivity methodologies and techniques for correlation are presented and critically evaluated for utility and applicability as predictive tools.

Early Studies

The first attempts to hydrogenate coal in the laboratory were carried out by Marcelin Berthelot (1) in 1868. The results of subsequent experiments were published by Ipatiev (2) and his co-workers in 1904, in which it was demonstrated that the yield of liquids via high pressure pyrolysis of numerous organic constituents could be markedly enhanced by application of hydrogen. Emil Fischer suggested in 1912 that if coking operations were carried out in a hydrogen atmosphere, an increased yield of hydrocarbons might result. This hypothesis was later confirmed by Franz Fischer and Keller (3), who distilled a bituminous coal in hydrogen under pressure and found that the tar yield was significantly enhanced. Further research on coal hydrogenation was carried out by Fischer and his co-workers at the Kaiser-Wilhelm Institute using for the most part sodium formate and carbon monoxide in the presence of water (4).

Research which would eventually lead to the first "commercial" process for coal liquefaction was in progress as early as 1910 under the direction of Friedrich Bergius. Bergius initially studied the conversion of cellulose and peat in the presence of water, and only later turned his attention to coal. Coals were found to behave in a similar fashion, and Bergius was granted a process patent in 1914 for conversion of coal and other carbonaceous substances. Much of the work of Bergius is summarized in a document published in 1925 (5). In this paper, Bergius first describes the effect of the nature of the coal on the yield of liquid and tars from coal and states that coals

containing more than 85% carbon (d.a.f.) gave unacceptably low yields and were hence unsuitable for hydrogenation. In laboratory investigations on a series of 29 British coals of different rank (lignite through anthracite) published in 1928, Graham (6) indicated that no such arbitrary reactivity division was justified. Correlations for hydrogenation yields with coal properties were attempted by Graham using such factors as ultimate carbon, C/H ratio, C/(H-(O/8)) ratio, moisture, oxygen, and fixed carbon. All correlations were deemed to be unsuitable. Beuschleim and Wright (7) in a study of the hydrogenation of 14 U.S. coals and later Gordon (8) also reported similar findings. Francis (9) suggested that the reactivity of coal toward oxidizing agents was an excellent measure of their reactivity towards hydrogen.

Macroscopic and Microscopic Coal Constituents

Bergius stated that fusain was the most difficult of the constituents of coal to liquefy. Shatwell and Bowen (10) reported the oil yield from a sample of hand-picked fusain from bituminous coal to be negligible. Wright and Sprunk (11) microscopically analysed the residues from batch hydrogenation of several different U.S. coals, and determined the relative reactivities of the various petrographic constituents. Both Gordon (12) and Heinze (13) stressed the need for reducing the fusain content of coals processed in continuous liquefaction plants in order to minimize handling problems in the solids/liquid separations unit operations. Other studies on the effect of the macroscopic properties of coal (vitrain, fusain, clarain, durain) were reported by Shatwell and Graham (14) and Horton et al. (15), with contradictory results.

The first systematic study on the effect of the macroscopic and microscopic coal constituents on coal reactivity was conducted at the Bruceton Bureau of Mines Research Station (now Pittsburgh Energy Technology Center of the US Department of Energy). An extensive treatise on the effect of the petrographic constituents on the reactivity of coal for direct hydrogenation was published by Fisher et al. (16) in 1942. As an integral portion of this research, the behavior of individual maceral groups was determined experimentally, and a correlation developed for liquefaction reactivity. A parity plot for predicted vs. actual yield of residue was presented by Fisher, where "residue" denoted the yield of acetone insolubles after reaction at 445 - 450 °C for 2 hours (initial hydrogen pressure of 2000 psi). Here, the yield of residue was predicted by assuming that the coal constituents would react as follows:

- ash and fusain = 100% residue
- opaque attritus = 38% residue
- all other constituents = 0% residue

While this correlation was deemed to be more adequate than previous relationships based solely on rank or carbon

content, the deficiencies in terms of chemical differences between macroscopic and microscopic coal constituents for coals of varying rank was recognized by these researchers.

The Work of Peter Given

During the 1970's, Professor Peter Given and his co-workers at Penn State University began a very extensive study of the effect of coal composition on coal reactivity utilizing 104 coals from the U.S. To date, a series of ten papers have been published concerning the coal reactivity studies of Given et al., of which two pertain directly to the subject of reactivity correlations. The first paper (17) dealt with correlations between properties of 104 coals from the Penn State/DOE coal sample bank and conversion of coal to ethyl acetate solubles measured after reaction at 400 °C for one hour in tetralin. This paper introduced the concept of cluster analysis to the subject of reactivity correlation. It was reported that partitioning the samples into three distinct groupings (clusters) markedly improved the total variation accounted for by the multiple linear regression models employed for correlation of conversion and coal properties. The groupings recommended had the following characteristics:

Group 1: medium sulfur, high rank

Group 2: high sulfur, medium rank

Group 3: low sulfur, low rank

The regression equations developed for correlation of liquefaction conversion and coal properties for each of these groups were as follows:

Group 1: $\text{Conv} = 34.8 R_o + 50.7 \text{ H/C} + 0.16 V + 30.5$

Group 2: $\text{Conv} = 0.86 \text{ VM} - 22.8 R_o + 1.39 S_t + 39.0$

Group 3: $\text{Conv} = 0.93 \text{ VM} + 0.28 \text{ TRM} - 1.7$

where: R_o = vitrinite reflectance

H/C = atomic hydrogen-to-carbon ratio

V = vitrinite content of coal

VM = volatile matter

S_t = total sulfur

TRM = total reactive macerals

The adequacies of these reactivity correlations, expressed as a percentage of the total variation in the data set explained by the model, were 80.0%, 79.2%, and 47.5% respectively. A later paper in the series (18) concentrated on the development of reactivity correlations for a set of 26 high volatile bituminous coals with high sulfur contents, and extended the models previously developed to include analyses of the liquefaction products and coal structural features. These structural features included the usual compositional parameters as well as data from FTIR, ^{13}C -nmr, and the products of oxidation with trifluoroperoxyacetic acid. No significant correlations between liquefaction yields and structural features of the coals were found from this study.

Reactivity Definitions

The traditional parameter that has been used for coal liquefaction reactivity correlations is the point-yield conversion. This parameter is defined by measuring the yield of some solvent-soluble material (THF, pyridine, toluene, etc.) at a fixed reaction time and fixed temperature. This single parameter has been widely utilized by many researchers as the dependent variable in reactivity correlations with coal properties such as volatile matter, H/C and O/C atomic ratios, vitrinite reflectance, maceral distribution, etc. (19,20,21,22,23,24,25,26). As has been recently demonstrated by Shin et al. (27), this parameter can provide meaningful correlations with coal properties for a narrow suite of reasonably homogeneous coals, but the correlations weaken significantly or even disappear if either the time or temperature is changed. Use of a rate constant as a correlational parameter for coal reactivity was proposed by Furlong (28) and Gutmann (29), and was found to be generally satisfactory for a particular suite of coals within a single rank. This parameter, however, also fails to hold if the temperature is changed (27). An attempt to derive a more universal parameter that could be employed for definition of coal reactivity was made by Shin et al. (30), who combined both static and dynamic reactivity parameters into a single variable.

Many of the compositional parameters utilized as independent variables in the work cited above represented derived coal properties rather than fundamental chemical features which, as pointed out by Neavel (31), limits their utility in correlational models. Instrumental techniques such as pyrolysis/mass spectrometry (32,33) ^{13}C -n.m.r., FTIR, and ^1H -n.m.r. have also been employed in an attempt to generate a larger data base of compositional information for use in correlation with reactivity. In some cases, the parameters developed from these data are derived from statistical techniques such as principal component and factor analysis, and thus have little if any interpretation or meaning chemically. In this regard, the later work of Neill, Shadle, and Given (34) represents a significant departure from this philosophy in that an attempt was made to correlate both liquefaction chemical properties and coal structural features with the observed liquefaction reactivity.

The lack of significance often found with single-parameter reactivity models has been interpreted to reflect the need for development of multi-parameter models containing functional dependence for reactivity on several compositional parameters. Recently, the use of activation energy as a fundamental parameter for correlation of liquefaction reactivity data has been proposed. Prasad (35) collected reported values for activation energies from other studies, and found a direct correlation between

hydroliquefaction activation energy and the H/C ratio of the coal. Shin et al. (36) measured the hydroliquefaction activation energies for conversion of 5 bituminous coals from the Argonne Premium coal collection to THF and toluene solubles. Correlation of these data with fundamental coal chemical properties as determined from ^{13}C -n.m.r (CP/MAS with dipolar dephasing) and ^1H -n.m.r. (CRAMPS) was successful in developing single parameter reactivity models with very high levels of significance (90%+) between the following variables:

Ea (toluene) <---> total oxygen
 Ea (THF) <---> aliphatic hydrogen
 Ea (toluene) <---> protonated aliphatic carbon

Observations and Conclusions

Coal is an extremely heterogeneous material, both from a macroscopic and microscopic point of view. Correlation of liquefaction reactivity with coal properties is, as a result, inherently difficult and any truly "universal" correlations that will be developed will need to be based on fundamental coal chemical and structural information. Lack of this type of information has been a severe limitation for all of the correlational efforts cited in this brief review. If truly predictive models are to be developed, basic data on coal structure will be invaluable. Choice of a reactivity definition employed as the dependent variable in these correlations is probably relatively arbitrary, and may be based totally on purely operational considerations (rate of reaction or extent of reaction) rather than any fundamental considerations. The role of pretreatment processes on reactivity modification (drying, grinding, etc) and mineral matter and matrix effects caused by organic/inorganic interactions needs to be better defined. This is especially true for low rank coals, where the inherently high reactivity of these materials can cause severe processing difficulties leading to artificially low levels of conversion.

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